Appendix C

Fate, Transport, and Effects of Critical Pollutants in the Lake Superior Basin

C.1 Adverse Effects of Persistent, Bioaccumulative, and Toxic Chemicals

Over the past 25 year, there has been considerable public and scientific concern regarding the effects of chemicals on wildlife and the potential for significant adverse effects on human health in the Great Lakes basin. Adverse effects range from immune system disease and reproductive problems in wildlife to subtle developmental and neurological impacts on children and fetuses. LaMP Critical pollutants are widely distributed in the environment both inside and outside of the Great Lakes basin. Lake Superior has no additional capacity to assimilate virtual elimination chemicals)these chemicals have already accumulated to levels that are of concern to human health and wildlife. All nine of the zero discharge demonstration pollutants have been reported to have the potential to disrupt endocrine function in humans (Table C-1) (Colborn et al., 1993). Many of the critical pollutants are potential human carcinogens.

Exposure to critical pollutants occurs predominantly through food consumption—especially of Great Lakes fish.

C.2 Critical Pollutant Behavior in Lake Superior

The lakes illustrate the familiar principle of conservation of mass, or stated another way, what you have retained within the ecosystem is equal to what goes in minus what comes out. Scientists and water quality managers are finding that looking at where chemicals are coming from can explain much about the presence of pollutants in Lake Superior. The mass of a certain chemical emitted from a source in a given year is called the source loading. The source can be an industrial facility, landfill, incinerator, leaking transformer, or even degassing from soils. As used in this document the term "source loading" is generally synonymous with discharges and emissions. Alternatively, the term "pathway" or "pathway loading" refers to transport mechanisms that describe, on a gross scale, the inflow and outflow of chemicals to the lake. Example pathways are atmospheric deposition and river inflows and outflows. The following discussion will show how reducing the source loadings of chemicals will reduce the pathway loadings to the lake and eventually cause levels in the water column to decrease.

The retention of chemicals in Lake Superior depends on the ease at which chemicals can exit the lake. The hydraulic retention time for Lake Superior is 174 years, with water flowing out through the St. Marys River. The actual rate at which Lake Superior responds to changes in chemical loadings is much faster due to contributions of several other removal pathways. Chemicals can volatilize to the atmosphere, attach to settling particles eventually to become buried in deep sediments, and degrade by chemical and biological processes. Chemicals enter Lake Superior by tributary inflows, overland flows such as agricultural and urban stormwater runoff, sewer overflows, industrial discharges, wet and dry atmospheric deposition, vapor exchange with the atmosphere and chemical exchange between the water column and sediment. The relative magnitudes of these processes depend on the properties of the chemical, nature of the source loadings, and physical factors controlling the transport of chemicals.

Most LaMP critical pollutants have certain common characteristics. They resist being dissolved in water, preferring instead to volatilize into the atmosphere. Thus volatilization from the lake, although counter intuitive for a chemical (e.g., mercury) that has a low vapor pressure, is an important process for many bioaccumulative chemicals. Many of the critical pollutants enter Lake Superior primarily

Table C-1. Potential Human Health Effects Associated with Pollutants of Concern
(USEPA, 1995; NLM, 1995; USEPA, 1994; Colborn et al., 1993)

	Potential Effects on Human Health					
Pollutant	**Cancer**	**Reproductive/ Restrictions**	**Neurological/ Behavioral**	**Immuno-logical**	**Endocrine**	**Other Noncancer**
Cadmium and compounds	Probable	!	!	!	!	Respiratory & kidney toxicity
Chlordane**	Probable	!	!	!	!	Liver toxicity
DDT/DDE **	Probable	!	!	!		Liver toxicity
Dieldrin**	Probable	!	!	!	!	Liver toxicity
Hexachloro-benzene**	Probable	!	!	!	!	Liver toxicity
α-HCH	Probable		!			Kidney & liver toxicity
Lindane	Probable	! γ-(HCH)	!	!	!	Kidney & liver toxicity
Lead and compounds	Probable	!	!	!	!	Kidney toxicity
Mercury and compounds **	*	!	!	!	!	Kidney toxicity
PCBs**	Probable	!	!	!	!	Liver toxicity
PAHs	Probable	!		!	!	Blood cell toxicity; liver & kidney toxicity
2,3,7,8-TCDF	Not class-ifiable	!		!	!	Liver toxicity
2,3,7,8-TCDD**	Probable	!	!	!	!	Integument toxicity
Toxaphene **	Probable	!	!	!	!	Cardiovascu lar effects; liver toxicity
Octachloro-styrene**	Not class-ifiable				!	Liver toxicity
Heptachlor-epoxide	Probable	!	!	!	!	Liver toxicity

* no data for inorganic mercury
possible carcinogen for methyl mercury
** Lake Superior Critical Pollutant targeted for zero discharge

through atmospheric deposition and leave primarily through volatilization. In addition to escaping in this manner, hydrophobic or "water-hating" chemicals avoid aqueous solution by attaching themselves to particles or organic materials and can settle out in sediments. Many also are inert to chemical or biological breakdown and thus persist for long periods in the environment. Their persistence allows them to drift in the atmosphere over great distances before they fall out in rainfall or attached to dust particles. They tend to be distributed widely among environmental media, becoming omnipresent in the environment, and thus enhancing the potential of human and wildlife exposure. Given the persistent presence of these critical pollutants in the environment, it is imperative that their sources be identified and controlled.

C.3 Estimating Lake Superior Response to Load Reductions

It is useful to consider where models are available, the anticipated changes in environmental levels from these management practices and/or loadings reductions. One question that might be asked is how long will it take for Lake Superior to recover if no action is taken versus how long it will take under various load reduction scenarios. An "input function" can be used to evaluate lake response time. An input function is a profile or plot of the pathway loadings of a chemical over time. An example input function for hexachlorobenzene (HCB) (Figure C.1) shows how the atmospheric deposition of HCB increased rapidly between 1945 and 1969. Atmospheric input functions can be obtained from the study of cores taken from peat bogs. Sediment cores, likewise, are used to obtain input functions for deep burial in sediments. Another useful piece of information to estimate the lake's response is a long-term plot of the concentration of the chemical in the lake. Declining levels of PCBs, DDTs, and chlorinated benzenes have been observed in water, fish, bird eggs, and sediments over the last 20 to 30 years (LTI, 1993).

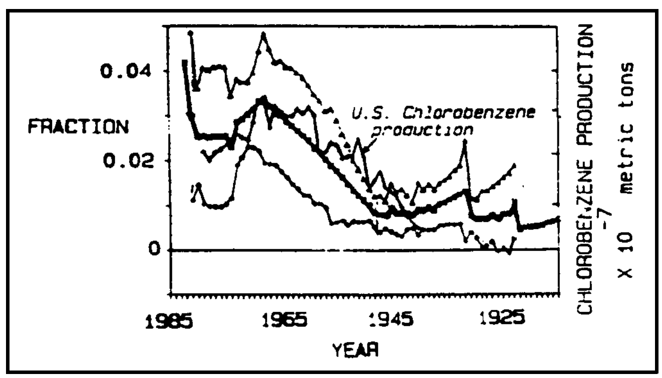

Figure C.1. Atmospheric source function for hexachlorobenzene (HCB) derived from peat bog cores taken from several sites in North America (Rapaport and Eisenreich, 1988).

Source functions are distinguished from input functions in that they chronicle long-term changes in chemical use and production. Historically, pathway loadings have been directly related to source loadings. As chemicals cycle through the environment pathway loadings will continue long after source loadings have ceased. For example, hexachlorobenzene's input function parallels the history of U.S. chlorobenzene production (Figure C.1). The input function for PCBs, likewise, reflects the history of PCB use in the United States. Although input functions are available for several chemicals, including PCBs, hexachlorobenzene, toxaphene, and DDT (Rapaport and Eisenreich, 1988), reliable, long-term, ambient lake monitoring data is generally wanting (LTI, 1993). PCBs are the only chemical for which both long-term monitoring data and an input function are available.

A mass balance model links an input function (or the sum of several input functions in the case of multiple input pathways) with water quality trends (Figure C.2). More detailed mass balance

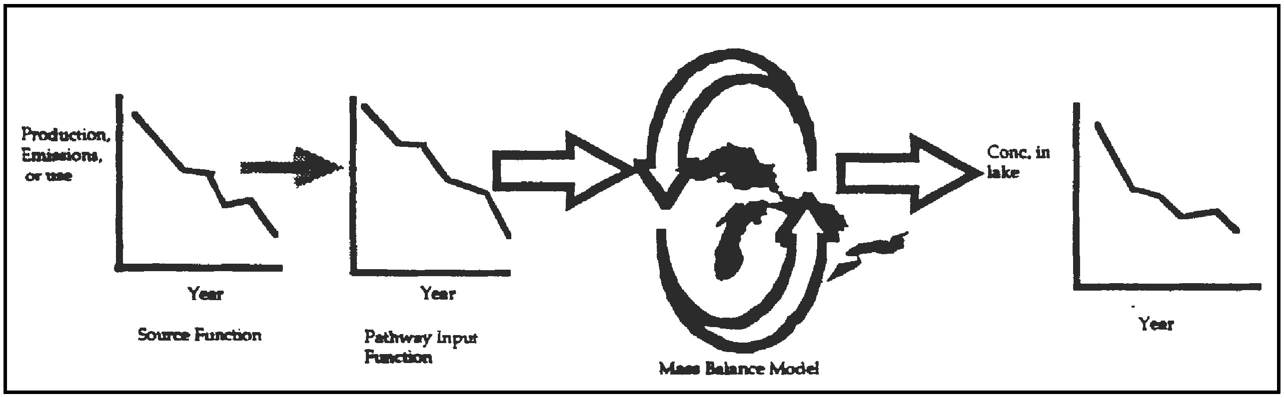

Figure C2. Mass balance model showing information requirements and model output. A more detailed model can also predict concentrations in biota and sediments.

models also predict responses in biota and sediments. The models are calibrated using existing data. Since models require information on atmospheric inputs, any water quality projections generated by the models must include a projection of the magnitude of future atmospheric deposition pathway loadings. Differences in the assumptions made by modelers can account for differences in water quality projections. Due to the necessity of assumption, no model can depict or predict the fate of persistent pollutants with high accuracy. Three mass balance models for PCBs in Lake Superior were considered. A well developed mass balance example is the PCB model prepared by Dr. D. Mackay of the University of Toronto for the IJC Virtual Elimination Task Force (VETF, 1993). Dr. Mackay has also used a similar model to determine a variety of scenarios for Lake Ontario where control of PCB loadings was investigated, both from what reductions were necessary to achieve desired goals (safe contaminant levels in lake trout) and what the delay is between action and change in environmental levels. This is important in order to frame public expectations, particularly in Lake Superior, where the large volume of the lake, cold temperatures and limited sedimentation prolong the availability of contaminants in the lake, ensuring that reductions will not be noted in the environment until well after the management activity has taken place.

The IJC VETF model included several pathways for pollutants to enter and exit Lake Superior. Modeled input pathways were shoreline discharges, wet and dry atmospheric deposition, direct absorption of PCBs from the atmosphere, and desorption from sediments. Removal from the water column was assumed to occur by outflow via the St. Marys River, sedimentation, deep burial, volatilization, and chemical and biological transformations. Simulation results show the likely response of PCBs in Lake Superior water column and sediments to several scenarios for loadings reductions (Figures C.3 and C.4). Cases investigated included no reduction in source loadings, and maximum, minimum, moderate, and vigorous reductions in loadings of PCBs from atmospheric and land sources. Resulting concentrations in water and sediment are projected over a 15-year time scale. The basic premise for this reduction scenario is that existing loadings (370 kg/yr) are initially at equilibrium with ecosystem levels. Since loadings have decreased over time, the snapshot model can provide an indication of future trends. The model proposed by the VETF for PCBs in Lake Superior suggests that no action will result in a 20 percent decrease in water by 2010, and a 40 percent decrease in sediment over the same time period. However the model does not provide information on the levels in biota, such as lake trout or herring gulls and bald eagles.

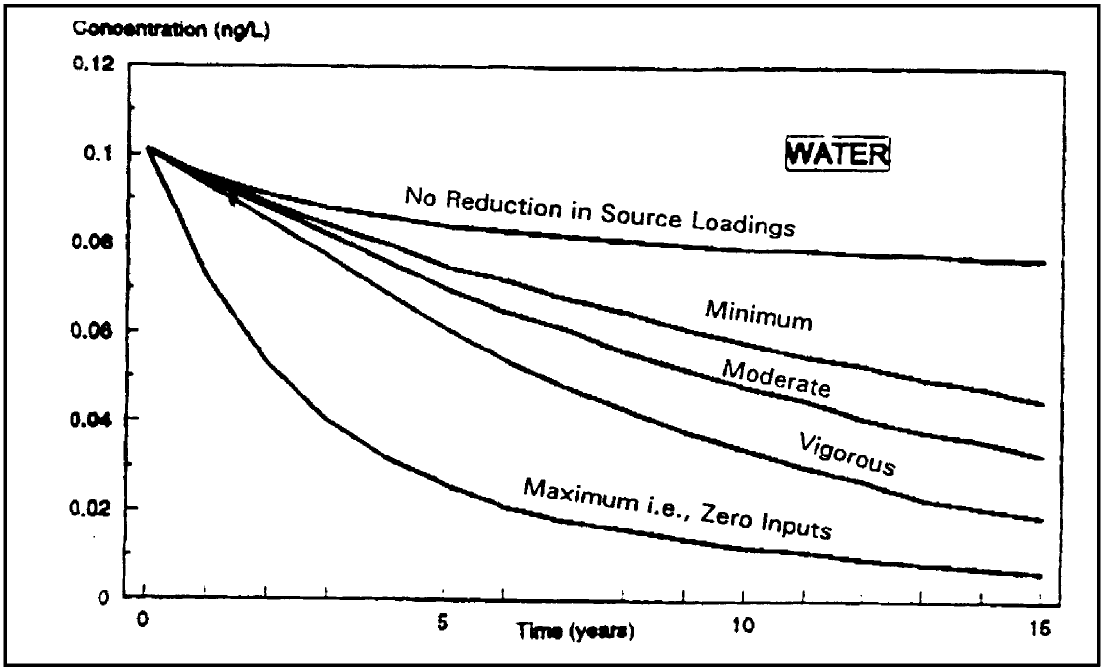

Figure C.3. Response time of PCBs in Lake Superior water from VETF (1993).

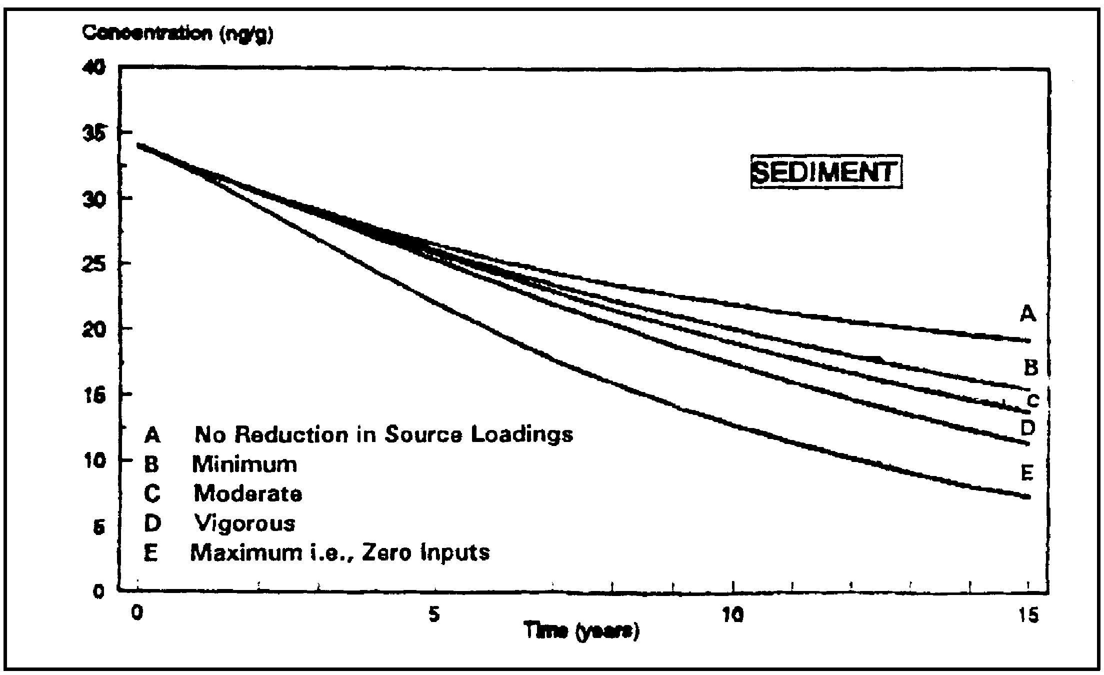

Figure C.4. Response time of PCBs in Lake Superior sediment from VETF (1993).

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No Reduction in Source Loadings: No measures are taken
Maximum: Zero inputs of PCBs from atmospheric and land sources
Minimum: Loadings of PCBs from atmospheric and land sources drop yearly by 5%
Moderate: Loadings of PCBs from atmospheric and land sources drop yearly by 8% and 10%, respectively
Vigorous: Loadings of PCBs from atmospheric and land sources drop yearly by 15% and 20%, respectively

Jeremiason et al. (1994) investigated the relative importance of various PCB removal pathways from Lake Superior by examining the contributions to the apparent removal half-life. They concluded that the largest input pathway to Lake Superior is atmospheric deposition and the largest removal pathway is volatilization. Figure C.5 shows that water column concentrations of PCBs have declined exponentially in Lake Superior at a rate of approximately 0.20 yr^{-1}, which is equivalent to an effective "half-life" of 3.5 years. The 3.5 year "half-life" is not the true half-life for PCBs in Lake Superior because the effects of declining atmospheric inputs during the period 1980 to 1992 were not considered in the calculation. The normal usage of the term "half-life" represents the time it would take for lake concentrations to decrease by half if all inputs ceased. The actual half-life for PCBs in Lake Superior might have come out to be less than 3.5 years if declining trends in atmospheric deposition had been assumed by Jeremiason and others (1994).

The authors concluded that the response time of Lake Superior was relatively rapid during the period investigated. Decreases in PCB water concentration levels between 1980 and 1992 were due primarily to decreases in the atmospheric input that occurred during this same period (Jeremiason et al., 1994). PCBs and several other persistent toxic substances, including lead and mercury, are migrating across North America via the so called "grasshopper effect", i.e., through successive volatilization, transport, deposition, and re-volatilization processes. The higher latitudes might constitute the ultimate sink for these chemicals due to the effect of lower temperature on the air-water and air-terrestrial exchange process.

Although atmospheric deposition to Lake Superior might continue to decrease, future trends in atmospheric deposition are purely speculative. In addition, there is no guarantee, nor did the authors promise, that reductions according to the 3.5 year effective half-life will continue into the future. The net magnitude of the atmospheric exchange process might decrease in the future as PCBs travel northward, increasing the relative importance of the slow process of exchange between sediments and the water column. This would have the effect of lengthening the effective half-life. PCB concentrations shown in Figure C.5 do not necessarily mean that Lake Superior is at equilibrium with respect to constant pathway loadings. The effect observed could also be caused by a slight declining trend in pathway loadings coupled with a slowing removal rate, due to the effect of increased contributions to the water column from historically discharged pollutants depurating slowly from sediments. Mass balance simulations for PCBs in Lake Ontario indicated that half-lives for PCBs might not remain constant over time but increase gradually until they converge at the maximum rate at which PCBs can be

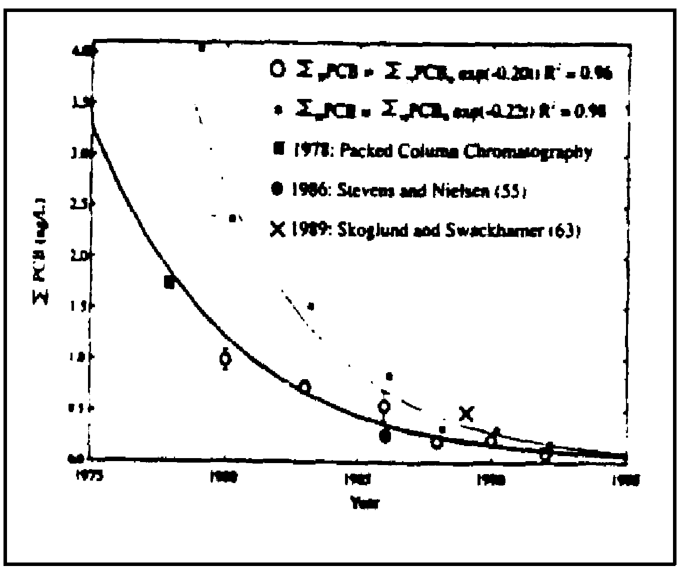

Figure C.5. PCB decline in Lake Superior waters from 1980 to 1992 (after Jeremiason et al., 1994). PCB concentrations in Lake superior, have declined over the last 20 years since manufacture ceased in 1978 (not shown). Up until the early 1980s, declines in lake concentrations were attributed largely to reductions in point source loadings and improved disposal practices. Recently, however, the rate of decline in PCB lake concentrations has slowed. Concentrations in the atmosphere, sediments, and fish have remained approximately the same since the early 1980s.

removed from the active sediment layer (Gobas et al., 1995). The PCBs in sediments, due to their slow response time relative to the exchange between the lake and the atmosphere, are almost always in disequilibrium with PCBs in the water column. The slow removal rate from contaminated sediments is consistent with their observed association with historic discharges. The rapid exchange between the water column and atmosphere means that Lake Superior waters, unlike sediments, respond rapidly to atmospheric inputs. Changes in water column concentrations can represent recent trends in pathway and source loadings.

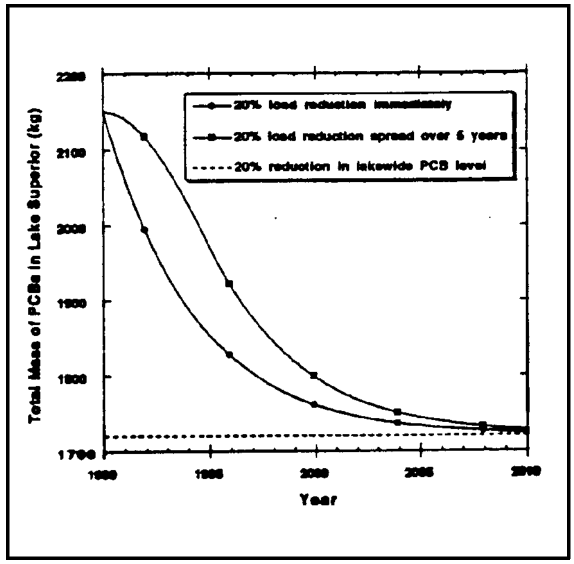

Figure C.6. Lake Superior Response to 20% load reduction in PCBs under two scenarios.

The final mass balance case study illustrates the effect of two reduction target schedules. The hypothetical example compares the response to an immediate 20 percent pathway loading reduction to that expected if the same loading reduction was spread out over 5 years. Figure C.6 shows the mass of PCBs in Lake Superior changing over time under the two reduction schedules. In the hypothetical case chosen, the lake was assumed to start out in 1990 at steady state with an initial mass of 2150 kg and a total PCB input from all pathways of 500 kg/yr. Sediments and biota were not modeled in this simplified example that used a time-invariant, first-order removal rate. The middle curve on the figure shows how the concentration in the lake would respond if a 20 percent load reduction had occurred in 1990. The top curve on Figure C.6 shows how the lake would respond to a 20 percent reduction spread out between 1990 and 1995 (e.g., 4 percent per year for 5 years). In either case, the lake will respond with a 20 percent reduction in open lake water PCB concentration (dotted line on Figure C.6). In Figure C.6 the lake appears to reach a 20 percent reduction somewhere shortly after the year 2010. The decline takes place gradually with a half-life of approximately three years. If the load reductions occur at a slower rate such as 4 percent per year for five years (top curve on Figure C.6), lake PCB levels will drop more slowly in the first 15 years; however, there is little difference in the curves by the year 2008. Both curves asymptotically approach the dotted horizontal line marking a 20 percent reduction in open water PCB concentration.

C.5 Summary

Several conclusions can be drawn from the PCB case studies:

- If atmospheric deposition inputs continue to decrease in the future, concentrations of PCBs in Lake Superior will also decrease without human intervention. The model proposed by the VETF for PCBs in Lake Superior suggests that no reduction in source loadings will result in a 20% decrease in water concentration levels by 2010, and a 40% decrease in sediment levels over the same time period (VETF, 1993).

- Less is known about how the no action alternative will affect other chemicals.

- The response time of Lake Superior waters for PCBs might be less than 3.5 years, but is almost certainly less than 10 years. Reductions in the net amounts of PCBs delivered to the lake, therefore, should produce rapid water quality benefits. A decrease in lake pollutant concentration corresponding to reductions in the amount of chemical entering the lake through various paths (e.g., a 20 percent reduction in total inputs means an eventual 20 percent reduction in lake concentration) will occur in theory for most of the other pollutants in less than a decade (LTI, 1993). It is more difficult, however, to predict concentrations in biota or when beneficial uses will be restored.

- Monitoring data for lake concentrations must be interpreted in conjunction with estimated trends in source loadings to adequately define the status of Lake Superior with respect to pollutant inputs. Source loading estimation might provide a more direct approach to pollutant management in Lake Superior due to the inherent uncertainties in mass balance models.

- Source load reductions can reduce lake concentrations but will not achieve a concentration of zero because we cannot control all of the inputs.

In summary, experience with PCBs indicates that the Lake Superior basin might respond rapidly to reductions in pollutant loadings. The concentrations of PCBs, and many other chemicals that have been banned or otherwise regulated, have declined significantly in the last 20 years. The declines have been in direct response to source loading reductions, indicating that Lake Superior can respond rapidly to management (LTI, 1993). Monitoring data for Lakes Superior and Michigan indicated that loss rates for PCBs are similar for both lake trout and the water column (LTI, 1993), suggesting that levels in some aquatic organisms can respond rapidly to pathway loading reductions in a manner similar to the water column. Some aquatic organisms (e.g., sculpins in Lake Ontario), however, respond very slowly to concentration declines in the water column (Gobas et al., 1995). Differences among organisms depend on age class, species, position in water column, lifestyle, and composition of diet. Evidence suggests that surface soils and atmospheric systems also respond rapidly to reductions in atmospheric pollutant loadings (Rapaport and Eisenreich, 1988). Sediment deposits, however, tend to respond more slowly.

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